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Crystalline and spectroscopic experimental study of the dinitromesithylen (DNM) compared with the theoretical results

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Abstract

The aim by our group is to understand the behaviour of the grouping methyl starting from the study of molecules having a great symmetry.

In this part of work, it is had the crystalline structure of the dinitromesitylen (DNM) who is solved starting from the diffraction of x-rays starting from a monocrystal at the ambient temperature. Parallel to the experimental study, we undertook theoretical calculations conformation of the insulated molecule of DNM by using the methods of the DFT (Density Functional Theory).Calculations of optimization of the molecular conformation of the DNM by using the chain of program GAUSSIAN03 and functional MPW1PW91, B3LYP level with the 6-311G and LANL2DZ bases gave a conformation Cs with results very close to the experiment for the lengths and the angles of bond. The computation results obtained starting from the base set (6-311G) and functional MPW1PW91 give for the conformation of Dinitromesitylen (DNM) a good agreement of about a 1.9% for the lengths of bond and 1.2% for the angles of bond compared with the results of the diffraction of x-rays.

Calculations of Raman and infra-red spectroscopy undertaken starting from the results of optimization by using same functional MPW1PW91 and B3LYP and the sets of bases 6-311G LanL2DZ led to the values of frequencies very close to the experimental results.

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Keywords: Diffraction ; DFT, Conformation ; Infrared.

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1. Introduction

The work which is presented here will complete the studies which are already initiated to understand better the behavior of radical CH_3 and the influence of steric jamming resulting from this substitution by dioxide of nitrogen which produce this substitution and concerning a crystallographic study of dinitromesithylen starting from the X-ray diffraction at room temperature. In contrast to the isotypes products known in the literature, diiodomesithylen and dibromomesithylen [1] which belong to the $P2_1/n$ with Z=4.The dinitromesithylen (DNM) crystallizes in the space group $P2_12_12_1$ with four molecules by cell by diffraction of X-rays at the ambient temperature and optimization calculations using the GAUSSIAN03 [2] program with the help of functional B3LYP and MPW1PW91.

2. Experimental Part

The recording of the intensities of diffracted rays from X-rays at room temperature using a single crystal of dimension 0.10 x 0.3 x 0.2 mm was performed with a Nonius Kappa CCD diffractometer from the center of diffraction of the University of Rennes 1 (France) using a two dimensional CCD detector charge coupled device.

Resolution of the crystal structure

The crystalline structure of dinitromesithylen determined from X-rays at room temperature 297 K was made with the help of the (WINGX [3], SIR92 [4]CRYSTALS [5]).The flatness of the molecule of DNM confirms the results already found in the literature conceding halogenomesithylen (TCM [6], TBM [7], TIM [8], DBM [1]).

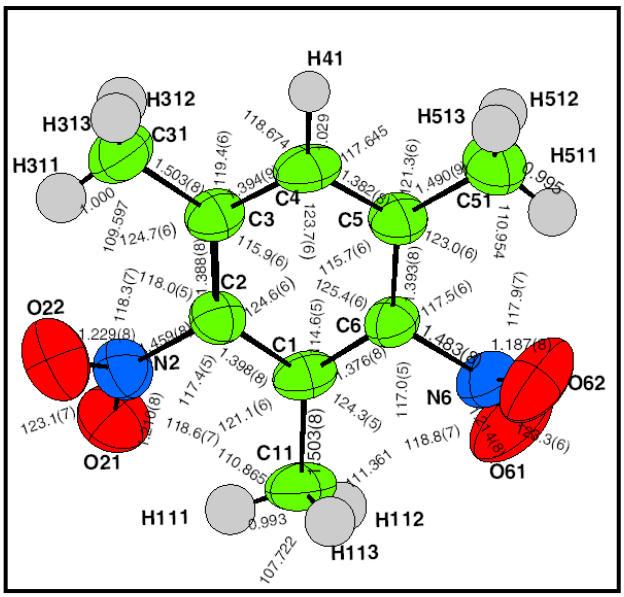

Fig1. Structure refinement of DNM at 293K .Displacement's ellipsoïd are drawn at the 50% probability level.

- The molecule of the dinitromesithylen with the orientation of the bond C-H of each methyl contained or very close to the average plane of the molecule consolidates its symmetry C_s.

- Only one of the two groupings methyl's surrounding the bond C_{ar}-H presents a bond C_{Me}-H contained in the average plane of the molecule with a variation of 3.38° compared to this average plane. These two groupings methyl's have each one on of their bonds oriented towards this hydrogen.

- The bond C_{31} - H_{312} contained roughly in the average plane of the molecule can be at the origin of a strong interaction of repulsive origin with H41 hydrogen from where great spacing of the angle C_3 - C_{31} - H_{312} = 113.3(3) ° and C_3 - C_4 - H_{41} = 120.7(2) ° and also the exit gold of the plane of the bond C4 - H41 with a variation of 0.41compared to this plane.

- The radical methyl located between two nitrogen dioxides is slightly disturbed by the interactions of two groups NO2 with a difference of 1.4 (4) ° of the angles C_{ar} - C_{ar} - C_{Me} adjacent with the bond C_1 - C_{11}. This difference is negligible 0.1(2) ° in the case of the isotopic dibromomesitylen of where same methyl is encircled by brome always in position ortho.

3. Molecular conformation calculated starting from the DFT of (DNM)

The calculation methods based on the functional density DFT, we made a calculation geometric optimization of the molecular conformation of the molecule of dinitromesithylen from two different functional B3LYP and MPW1PW91 and two bases (6-311, Lanl2DZ) to achieve results very close to those obtained experimentally from the X-ray diffraction.

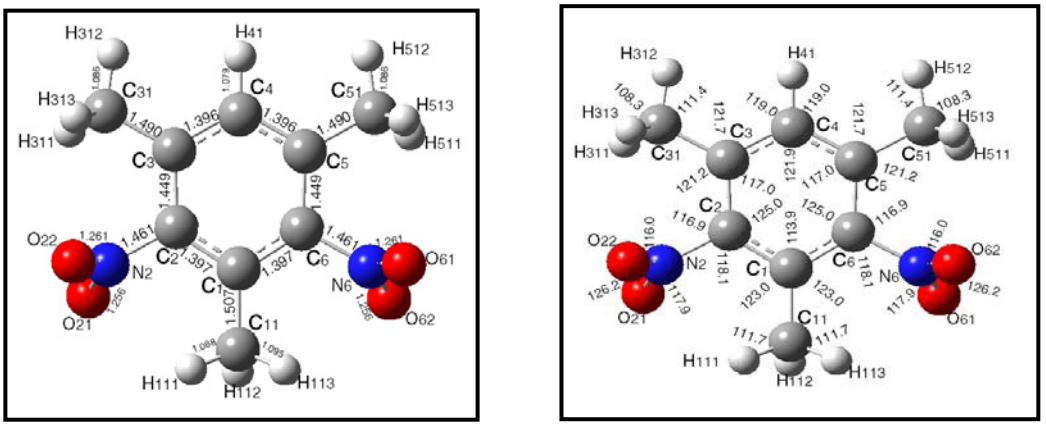

Fig.2. Molecular conformation of DNM (a) bond length (Å) ; (b) bond angle (°) found from DFT (B3LYP, 6-311G) and (B3LYP; Lanl2DZ) respectively.

4. Comparison of theoretical and experimental results

Tables 1 and 2 summarize in a general way the agreements between the values obtained in experiments (bond angles and bond lengths) and these calculated by the DFT.

Table.1.The experimental (X-ray) and theoretical (B3LYP/Lanl2DZ; MPW1PW91/6-311G) bond angles (º) for dinitromesithylen

Angle(˚)	(X-ray)	B3LYP/LanD2Z	Agreement(%)	MPW1PW91/6-311G	Agreement(%)
C1-C2-C3	124.3 (4)	125.0	0.56	124.9	0.48
C2-C3-C4	115.4 (4)	117.0	1.39	117.1	1.47
C3-C4-C5	124.3 (4)	121.9	1.93	121.8	2.01
C4-C5-C6	115.5 (5)	117.0	1.30	117.1	1.38
C5-C6-C1	125.5 (4)	125.0	0.40	124.9	0.48
C6-C1-C2	115.0 (4)	113.9	0.96	114.0	0.87
C11-C1-C2	121.8 (4)	123.0	0.98	123.0	0.98
C11-C1-C6	123.2 (4)	123.0	0.16	123.0	0.16
C31-C3-C2	124.5 (4)	121.2	2.65	120.7	3.05
C31-C3-C4	120.1 (4)	121.7	1.33	122.1	1.66
C51-C5-C4	120.3 (4)	121.7	1.16	122.1	1.50
C51-C5-C6	124.2 (4)	121.2	2.41	120.7	2.82
N2-C2-C1	117.9 (4)	118.1	0.17	118.2	0.25
N2-C2-C3	117.8 (4)	116.9	0.76	116.9	0.76
N6-C6-C1	117.1 (4)	118.1	0.85	118.2	0.94
N6-C6-C5	117.4 (4)	116.9	0.43	116.9	0.43
O21-N2-C2	117.7 (5)	117.9	0.17	117.5	0.17
O21-N2-O22	123.7 (5)	126.2	2.02	126.7	2.42
O22-N2-C2	118.6 (5)	116.0	2.19	115.7	2.44
O61-N6-C6	118.8 (5)	117.9	0.76	117.5	1.09
O61-N6-O62	123.1 (5)	126.2	2.52	126.7	2.92
O62-N6-C6	118.0 (5)	116.0	1.69	115.7	1.94
H41-C4-C3	120.7 (2)	119.0	1.41	119.1	1.32
H41-C4-C5	114.8 (2)	119.0	3.66	119.1	3.74

Table .2. The experimental (X-ray) and theoretical (B3LYP/6-311G; MPW1PW91) bond distances (A˚) for dinitromesithylen.

Bond (A˚)	(X-ray)	B3LYP/6-311G	Agreement (%)	MPW1PW91/6-311G	Agreement (%)
C1-C6	1.373(6)	1.397	1.7	1.392	1.4
C6-C5	1.390(6)	1.449	4.2	1.446	4.0
C5-C4	1.381(6)	1.396	1.1	1.391	0.7
C4-C3	1.393(6)	1.396	0.2	1.391	0.1
C3-C2	1.399(5)	1.449	3.5	1.446	3.4
C2-C1	1.398(5)	1.397	0.07	1.392	0.4
C2- N2	1.460(6)	1.461	0.07	1.452	0.5
C6-N6	1.481(6)	1.461	1.3	1.452	1.9
N2-O21	1.219(5)	1.256	3.0	1.245	2.1
N2-O22	1.216(5)	1.261	3.2	1.250	2.8
N6-O62	1.184(5)	1.256	6.0	1.245	5.1
N6-O61	1.212(5)	1.261	4.0	1.250	3.1
C1-C11	1.508(5)	1.507	0.07	1.498	0.7
C3-C31	1.507(5)	1.490	1.1	1.480	1.8
C5-C51	1.488(6)	1.490	0.1	1.481	0.5
C4-H41	1.000(5)	1.079	7.9	1.078	7.8

Molecular conformation obtained by functional of calculus B3LYP has the greatest stability with energy of minimal formation this conformation found values on the bonds angles very close to the experimental results. The computation results of this functional calculus concerning the bonds lengths were taken into account at the time of the comparisons with the experiment. Among other theoretical calculations undertaken, functional of calculus MPW1PW91 (6-311G) found the best results over the bonds lengths close to the experiment.

The theoretical of calculations from the B3LYP (Lanl2DZ) have found better results for the angles (0.18 %) compared to the functional MPW1PW91 (6-311G).

- The calculation of quantum mechanics confirms the flatness of the skeleton of the molecular conformation with the plane of the molecule found by the X-ray diffraction.
- Two hydrogen of two methyl's C_{31} and C_{51} in the molecular conformation Cs contained in the average plane of the molecule are oriented towards the bond hydrogen C_4 - H_{41} These two hydrogen are slightly located on either side of said plane with dihedral angles of C_{ar}-C_{ar}-C_{Me}-H = ± 6.4 °.
- All hydrogen of C_{11} methyl ranging between two nitrogen dioxides are out of the average plane of the molecule.
- In the molecular experimental conformation one hydrogen methyl is contained in the plane of the molecule-oriented towards that hydrogen C_{ar}- H.
- The gap variations between the experimental values with those obtained from the quantum chemistry could be attributed to the intermolecular interactions.

5. Infrared Spectroscopy of DNM

Infrared absorption spectrum has been made in the physics laboratory of solid (University Constantine1) at the ambient temperature. The analysis and processing of raw data collected from infrared spectroscopy are treated with the ORIGIN [9] chain of program.

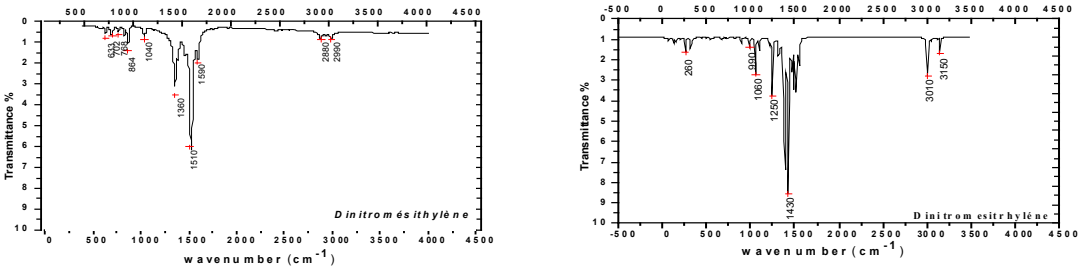

Fig. 3. (a) Experimental infrared Spectra of DNM at293K ;(b) Theory infrared spectra of DNM (MPW1PW91/ 6-311)

6. Conclusion

- The study of dinitromesithylen is to understand better the effect of the substitution dioxides of nitrogen and methyl's on the rest of the molecule.
- Both functional MPW1PW91 and B3LYP led to similar results.
- The crystal structure of dinitromesithylen is determined from X- rays at room temperature 297K and crystallizes in the space group $P2_12_12_1$ with Z=4.
- One of the two methyl's groups surrounding the bond Car-H presents one bond C_{Me}-H contained in the plane of molecule.

- The radical methyl located between two nitrogen dioxides is slightly disturbed by the interactions of two groups NO_2 with a difference of 1.4 (4) ° of the angles adjacent C_{ar}- C_{ar}- C_{Me} with the bond C_1-$C_{11.}$
- The flatness of the molecule found from the X-rays diffraction is found from the calculations of quantum mechanics.
- The allocation of different modes of vibration of the molecule has shown from frequencies obtained experimentally and theoretical calculations of differences of few cm^{-1} hence the importance of handling at low temperatures.

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